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(54) **PRODUCTION OF RESIN HAVING HIGH WATER ABSORPTION PROPERTY**

(57)Abstract:

PURPOSE: To provide the production method of a resin having high water absorption property, capable of efficiently producing a water absorbing resin having high water absorption rate and/or highly water absorbing ability.

CONSTITUTION: A group of base polymer particles having water absorbing property, comprising ≥ 60 wt.% of particles having $\leq 70\mu\text{m}$ particle diameters is mixed by an agitating blade under stirring and/or fluidized with an air flow, the group of base polymer particles is granulated into a group of granules having prescribed particle diameters in the presence of a binder and a cross- linking agent and the surface of each granule in the group of the granules is cross-linked to produce a resin having high water absorption property. The resin having high water absorption property is produced by blending the group of base polymer particles having a water absorbing property, comprising ≥ 60 wt.% of particles having $\leq 70\mu\text{m}$ particles diameters under stirring and/or fluidizing the group with an air flow, granulating the group of base polymer particles in the presence of a binder into a group of granules having given particle diameters and then cross-linking the surface of each granules in the group of the granules in the presence of a cross-linking agent.

* NOTICES *



- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The manufacturing method of the water-absorbing resin characterized by making the front face of each granulation object in this granulation **** construct a bridge while carrying out stirring mixing with an impeller, or making the base polymer particle group in which a particle with a particle size of 70 micrometers or less has the absorptivity which is 60 % of the weight or more fluidize according to an air current and corning this base polymer particle group to granulation **** of predetermined particle size under existence of a binder and a cross linking agent.

[Claim 2] The manufacturing method of the water-absorbing resin characterized by carrying out stirring mixing with an impeller, or making the base polymer particle group in which a particle with a particle size of 70 micrometers or less has the absorptivity which is 60 % of the weight or more fluidize according to an air current, corning this base polymer particle group to granulation **** of predetermined particle size under existence of a binder, and subsequently making the front face of each granulation object in this granulation **** construct a bridge under existence of a cross linking agent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Industrial Application] About the manufacturing method of a water-absorbing resin, in detail, this invention makes the start sanitary goods, such as sanitary items and a disposable diaper, and relates to the manufacturing method of the water-absorbing resin which can be used

for the application for which maintenance of the liquid which absorbed water is needed in broad fields, such as medical supplies and a soil water retention agent.

[0002] [Description of the Prior Art] Conventionally, absorptivity resin is used for broad fields including sanitary goods, such as a sanitary napkin and a disposable disposable diaper. Although a large water absorption scale factor, a large water absorption rate, dipping nature, and large gel strength are demanded especially in order to avoid the problem which gives displeasure, such as urine leakage, when using absorptivity resin for sanitary goods, it is very difficult to satisfy these properties to coincidence.

[0003] For example, as a means which raises a water absorption rate, the approach of making particle size of absorptivity resin small, the approach of raising the crosslinking density of the front face of absorptivity resin, the approach of enlarging surface area of absorptivity resin, etc. are mentioned. However, when particle size is generally made small, since absorptivity resin tends to produce an "insoluble" phenomenon and gel blocking by contacting urine, a water absorption rate falls. Then, the approach of raising the crosslinking density of the front face of above-mentioned absorptivity resin is proposed as a technique which raises a water absorption rate, without reducing a water absorption scale factor (scale factor of the water absorption weight to absorptivity resin weight). However, since many of absorptivity resin manufactured by this technique contains many fines, suspension of impalpable powder arises and it has a bad influence on work environment. Moreover, it is easy to produce an insoluble phenomenon in the case of water absorption, and has problems, such as causing the fall of absorptivity ability. Although removal by the classification of impalpable powder can be considered as the solution approach of this problem, since it is uneconomical, it is not desirable.

[0004] On the other hand, a granulation is mentioned as an approach of enlarging surface area of absorptivity resin. The approach about the granulation of absorptivity resin is indicated by JP,4-3411,B and JP,4-3412,B. The approach indicated by this official report is the approach of carrying out homogeneity mixing of absorptivity resin and the aqueous liquid, and carrying out crushing granulation of the obtained mixture using special mixers, such as a high-speed moving-vane mold mixer or an air mixer. However, although improved, in order that the handling as fine particles may produce ***** and an insoluble phenomenon to the original small particle before a granulation object corning and may cause gel blocking further in the case of water absorption, as for the granulation object obtained by the above-mentioned approach, it has the problem that absorptivity ability falls.

[0005] Moreover, the approach about the granulation of absorptivity resin is indicated by JP,2-227435,A. The approach indicated by this official report leads the absorbent base polymer in which it has 30ml [g] or more ordinary pressure liquid absorption ability, and 40 % of the weight or more has particle size distribution 150 micrometers or less, excluding a bigger particle than 300 micrometers to a mixed zone, contacts the front face of a base polymer to a cross linking agent water solution and homogeneity, and corns the absorbent polymer constituent which carries out high-speed mixing of these, and has the rate of absorption for 20 or less seconds. By the above-mentioned corning method, 1 - 20% of the weight of the cross linking agent water solution is used to the absorbent base polymer, and each absorptivity base polymer is corned according to an operation of the water in this water solution. However, in the above-mentioned corning method, since the binder is not used, only with the above-mentioned water, a granulation becomes inadequate and various problems arise. The mechanical strength of the granulation object obtained is weak, for example, since the particle over which the bridge was

corned and constructed is destroyed by the granulating machine during granulation, and expression of the part non-constructed a bridge takes place or it is easy to disassemble a granulation object into the primary particle of a basis at the time of water absorption, specifically, water absorption physical properties have the problem that it is not what should not necessarily be satisfied.

[0006] Therefore, the purpose of this invention is to offer the manufacturing method of the water-absorbing resin which can manufacture efficiently absorptivity resin with a high-speed water absorption rate and/or the high water-absorption-power force.

[0007] [Means for Solving the Problem] this invention persons came to complete header this invention for the ability of the above-mentioned purpose to be attained by corning the base polymer particle group which has specific particle size distribution, and making it construct a bridge, as a result of repeating research wholeheartedly, in order to develop the manufacturing method of absorptivity resin.

[0008] That is, this invention offers the approach (hereafter, in calling it "the 1st invention", it says this approach) of the following **, and the approach (hereafter, in calling it "the 2nd invention", it says this approach) of the following **.

[0009] ** The manufacturing method of the water-absorbing resin characterized by making each granulation object in this granulation **** construct a bridge while carrying out stirring mixing with an impeller, or making the base polymer particle group in which a particle with a particle size of 70 micrometers or less has the absorptivity which is 60 % of the weight or more fluidize according to an air current and corning this base polymer particle group to granulation **** of predetermined particle size under existence of a binder and a cross linking agent.

[0010] ** The manufacturing method of the water-absorbing resin characterized by carrying out stirring mixing with an impeller, or making the base polymer particle group in which a particle with a particle size of 70 micrometers or less has the absorptivity which is 60 % of the weight or more fluidize according to an air current, corning this base polymer particle group to granulation **** of predetermined particle size under existence of a binder, and subsequently making the front face of each granulation object in this granulation **** construct a bridge under existence of a cross linking agent.

[0011] Hereafter, the manufacturing method of the water-absorbing resin which is the 1st invention of this invention is explained to a detail. 50-1 micrometer of base polymer particle groups used for this invention is the particle group in which a 30-1-micrometer particle has preferably a fine particle size which is 80 - 100 % of the weight still more preferably 70 to 100% of the weight 60% of the weight or more still more preferably preferably the particle size of 70 micrometers or less. Since the surface area of the granulation object with which a granulation object becomes easy to collapse, and is obtained is small while there being few contacts of a base polymer comrade that particle-size the particle of 70 micrometers or less is less than 60 % of the weight since the surface area of each base polymer particle is small, and being hard coming to corn, it is hard to obtain a high water absorption rate.

[0012] The particle which consists of a well-known polymer which absorbs water, swells a lot of water in underwater as each base polymer particle which constitutes the above-mentioned base polymer particle group, and forms a hydrogel can be mentioned preferably. As this polymer, the polymer which has a carboxyl group is desirable, for example, the hydrolyzate of the hydrolyzate

of a starch-acrylonitrile graft copolymer, the neutralization (part) object of a starch-acrylic ester copolymer, the saponification object of a vinyl acetate-acrylic ester copolymer, an acrylonitrile copolymer, or an acrylamide copolymer, a polyvinyl alcohol denaturation object, partial neutralization polyacrylate, an isobutylene-maleic-anhydride copolymer, etc. are mentioned, and it can use as independent or two or more sorts of mixture on the occasion of use.

[0013] Moreover, although the above-mentioned base polymer particle may have the structure of cross linkage by the cross linking agent, its polymer which does not have the structure of cross linkage by the cross linking agent preferably is desirable. If the crosslinking density of a polymer is large, although a granulation is made, its mechanical strength of a granulation object is weak, and since it rose-**-comes to be separately easy by contacting water and urine, it is not desirable.

[0014] As an approach of obtaining the above-mentioned base polymer particle group efficiently, it is directly obtained in a well-known polymerization method by selecting the various conditions at the time of a polymerization, for example, a dispersant kind, dispersant concentration, an impeller, a stirring rotational frequency, etc. Moreover, when there are many particles of the particle diameter exceeding the particle size of 70 micrometers in the particle group obtained with an above-mentioned well-known polymerization method, it can obtain by carrying out grinding and/or classifying etc.

[0015] Although the mixed liquor of water, and a hydrophilic organic solvent and water, a water soluble polymer, etc. are mentioned, since the mechanical strength of the granulation object obtained especially increases as a binder which can be used in this invention, for example, the water soluble polymer solution made to dissolve a water soluble polymer in water or said mixed liquor is mentioned preferably. The concentration of the above-mentioned water soluble polymer in the above-mentioned water soluble polymer solution has 10 or less desirable % of the weight. If the concentration of a water soluble polymer exceeds 10 % of the weight, since the viscosity of a binder will become high and adjustment and spraying of a binder will become difficult, it is not desirable.

[0016] Moreover, when the above-mentioned base polymer particle group contains water, the water can be used as all or some of a binder. When the water content of the above-mentioned base polymer particle group is 20 - 70 % of the weight preferably 10% of the weight or more in that case, the water which this above-mentioned base polymer particle group contains can be made all [the above-mentioned binder].

[0017] As the above-mentioned hydrophilic organic solvent, the mono-ether of low-grade glycols, such as lower alcohol, such as a methanol, ethanol, and propanol, ethylene glycol, and propylene glycol, a low-grade glycol, and lower alcohol, a glycerol, an acetone, etc. are mentioned.

[0018] As the above-mentioned water soluble polymer, polyacrylic acid, a polyacrylic acid metal salt, a carboxymethyl cellulose, hydroxyethyl cellulose, a polyethylene glycol, polyvinyl alcohol, etc. are mentioned.

[0019] In this invention, although especially the amount of the above-mentioned binder used is not limited, as the above-mentioned binder, the amount of the water used in the case of using water, the above-mentioned mixed liquor, or the above-mentioned water soluble polymer solution is the 20 - 500 weight section preferably to the base polymer particle group 100 weight section, and is the 40 - 200 weight section more preferably. A granulation is inadequate in the

amount used being under 20 weight sections, and if it may remain so much and the 500 weight sections are exceeded, without corning each base polymer particle, for a **** reason, it is not desirable in time amount great to desiccation.

[0020] Moreover, as a binder, the addition of the above-mentioned water soluble polymer in the case of using the above-mentioned water soluble polymer or the above-mentioned water soluble polymer solution has desirable 0.001 - 10 weight section to the base polymer particle 100 weight section, and is 0.005 - 5 weight section more preferably. If there is less amount used than the 0.001 weight section, a granulation is inadequate, and it is not desirable in order that a water soluble polymer may check absorptivity ability, if it may remain so much and 10 weight sections are exceeded, without corning a base polymer.

[0021] It is not restricted, for example, the following compound etc. is mentioned, and especially the cross linking agent that can be used in this invention can choose and use the cross linking agent which does not react to mutual [one sort or two sorts or more of] from the group which consists of the following compound.

[0022] Ethylene glycol, a diethylene glycol, triethylene glycol, (Pori) Tetraethylene glycol, a glycerol (Pori), propylene glycol, Diethanolamine, triethanolamine, polyoxypropylene, Polyhydric alcohol, such as an oxyethylene-oxypropylene block copolymer, a pentaerythritol, and a sorbitol; (Pori) Ethylene glycol diglycidyl ether, Glycerol poly glycidyl ether, diglycerol poly glycidyl ether, (Pori) Sorbitol polyglycidyl ether, pentaerythritol poly glycidyl ether, Poly glycidyl ether compounds, such as propylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether; 2 and 2-screw hydroxymethyl butanol-tris [3-(1-aziridiny) propionate], Halo epoxy compounds, such as poly aziridine compound; epichlorohydrin, alpha-methyl full OROHI drine compounds, etc., such as 1 and 6-hexamethylene diethylene urea and the diphenylmethane-screw -4, 4'-N, and N'-diethylene urea; Ethylenediamine, diethylenediamine, The poly isocyanate compounds, such as polyamine compound;2, such as a TORIECHIREN tetra-amine, a tetra-ethylene PENTA amine, a pentaethylene hexa amine, and polyethyleneimine, 4-toluylene di-isocyanate, and hexamethylene di-isocyanate; Zinc, calcium, The mineral salt or organic metal salt which produces multicharged ion, such as magnesium and aluminum.

[0023] Moreover, also in the above-mentioned compound, especially the compound that has two functional groups is desirable, and one or more sorts of compounds chosen from the group which especially specifically consists of a diethylene glycol, triethylene glycol, a polyethylene glycol, a glycerol, polyglycerin, propylene glycol, diethanolamine, triethanolamine, polyoxypropylene, an oxyethylene-oxypropylene block copolymer, a pentaerythritol, and a sorbitol are used preferably.

[0024] The amount of the above-mentioned cross linking agent used has desirable 0.01 - 30 weight section to the base polymer 100 weight section, and its 0.1 - 10 weight section is more desirable. If the crosslinking density of the granulation object obtained as the amount of cross linking agents is under the 0.01 weight section becomes small, a water absorption rate falls by gel blocking and the amount of cross linking agents exceeds 30 weight sections, since crosslinking density becomes high too much and a water absorption rate and a coefficient of water absorption fall, it is not desirable.

[0025] And it can set at the time of use of the above-mentioned cross linking agent, and can use as a solution dissolved or diluted to solvents, such as water. As for the concentration of the above-mentioned cross linking agent in this solution, it is desirable to consider as 1 - 20% of the

weight of the range. In addition, when water is used as the above-mentioned solvent in the 1st invention, this water acts also as a binder.

[0026] It ** and the manufacturing method of the water-absorbing resin of this invention (the 1st invention) carries out stirring mixing of the above-mentioned base polymer particle group with an impeller, or while making it fluidize according to an air current and corning this base polymer particle group to granulation **** of predetermined particle size by above-mentioned binder and above-mentioned cross linking agent's existence-ization, it is characterized by making each granulation object in this granulation **** construct a bridge.

[0027] The well-known granulating machine which has an impeller can perform suitably stirring mixing by the impeller of the above-mentioned base polymer particle group. Specifically, a crushing granulating machine, such as kneaders, such as stirring mold tumbling granulator, such as "vertical granulator [Powrex Make]", and a kneader, and a "flash plate mill" [the Fuji Paudal make], etc. is mentioned.

[0028] Moreover, fluidization by the air current of the above-mentioned base polymer particle group can be suitably performed by the well-known approach. The approach of performing using the fluid bed equipment which is equipment which a gas is fed [equipment] for the particle in a cylinder through a straightening vane from the lower part of a packed bed, and makes a particle group specifically flow etc. is mentioned. Here, fluidization shows the condition that the particulate matter was pressured upwards by the air current and has suspended in a gaseous phase. Moreover, the gas used as an air current is a well-known gas, for example, air, nitrogen, etc. are mentioned.

[0029] Moreover, in this invention, although either the above-mentioned stirring mixing and fluidization may perform above-mentioned granulation and bridge formation, it is desirable to carry out by performing the above-mentioned stirring mixing and fluidization to coincidence. In order to perform the above-mentioned stirring mixing and fluidization to coincidence, it can carry out using the granulating machine which has a stirring mixing function by the impeller, and a flow function by the air current, and, specifically, can carry out using the rolling fluidized bed granulator which is equipment which included the function of centrifugal rolling granulation and a stirring granulation in fluidized bed granulators, such as a multiplexer (Powrex Make) and a new quince riser (Fuji Paudal make).

[0030] The above-mentioned binder and the above-mentioned cross linking agent are added in the above-mentioned base polymer particle group, it is performed by the above-mentioned stirring mixing and/or the above-mentioned fluidization, two or more above-mentioned base polymer particles gather according to an operation of the above-mentioned binder, and the granulation of the above-mentioned base polymer particle group serves as a granulation object. Under the present circumstances, a bridge is constructed over the front face of each granulation object by this granulation and coincidence. In addition, the above-mentioned bridge formation may not be limited only to the front face of the above-mentioned granulation object, for example, the bridge may be constructed over the front face of the above-mentioned base polymer particle etc.

[0031] Here, especially the sequence of the above-mentioned addition, and the above-mentioned stirring mixing and/or fluidization is not limited. Moreover, when the base polymer particle group to be used has above-mentioned water content (10 % of the weight or more), especially the thing for which a binder is added does not require.

[0032] Since addition of the above-mentioned binder and the above-mentioned cross linking agent can be performed by the approaches of spraying, such as a well-known approach, for example, a rotation disc method, a pressure nozzle method, and 2 fluid nozzle process, or the approach of adding directly in the above-mentioned base polymer particle group, can adjust the diameter of a drop especially easily, can atomize a hyperviscous binder and can moreover atomize it with low voltage, it is desirable to use 2 fluid nozzle process. Moreover, you may add according to an individual, and the above-mentioned binder and a cross linking agent may carry out homogeneity mixing, and may be added together.

[0033] Moreover, the above-mentioned fluidization can be performed within the same equipment as addition by the above-mentioned spraying by performing the above-mentioned fluidization using fluidized bed granulator. The above-mentioned fluidized bed granulator can mean the equipment which attaches the nozzle which makes fluid bed equipment atomize a binder, and the particulate matter currently fluidized is made to corn by contacting the spraying drop of a binder, for example, "WSG/WSG [Powrex Make]", the "powder coating machine GPCG" [Powrex Make], "glow MAKKUSU" [the Fuji Paudal make], etc. can be mentioned.

[0034] Moreover, when the above-mentioned rolling fluidized bed granulator is used, the above-mentioned stirring mixing, fluidization, and addition can be performed to coincidence.

[0035] Although the temperature and time amount in the case of above-mentioned granulation and bridge formation can be suitably chosen according to the class of the base polymer and binder to be used, a cross linking agent, and granulating machine, the range of them is usually 25-150 degrees C, and the range of them is 25-100 degrees C more preferably. Moreover, the time amount in this case has 10 - 120 desirable minutes.

[0036] It is the aggregate of a particle with which two or more above-mentioned base polymer particles gathered, and were formed, and a bridge is constructed over the front face of the above-mentioned granulation object, and the granulation object which are obtained by carrying out like **** has predetermined particle size, and it can carry out drying this remaining as it is or if needed etc., and it can be used for it as a water-absorbing resin. The 70-1500 micrometers of the above-mentioned predetermined particle size are 100-1000 micrometers more preferably. Since it will be easy to receive constraint by particle size when using for various applications if it is easy to produce an insoluble phenomenon to be less than 70 micrometers and exceeds 1500 micrometers, it is not desirable.

[0037] Subsequently, the manufacturing method of the water-absorbing resin which is the 2nd invention of this invention is explained. In addition, especially about the point which is not explained in full detail, it is the same as that of the 1st invention mentioned above.

[0038] Carry out stirring mixing with an impeller, or the manufacturing method of the water-absorbing resin which is the 2nd invention of this invention makes the above-mentioned base polymer particle group fluidize according to an air current, corns this base polymer particle group to granulation **** of predetermined particle size under existence of the above-mentioned binder, and is characterized by subsequently making the front face of each granulation object in this granulation **** construct a bridge under existence of the above-mentioned cross linking agent. That is, the 2nd invention of this invention is corned like the 1st above-mentioned invention under existence of the above-mentioned binder, and, subsequently makes the front face of the obtained granulation object construct a bridge under existence of a cross linking agent.

[0039] Bridge formation of the front face of the granulation object with which the above was obtained can be used without restricting especially a well-known approach. For example, the method of adding the water solution of the above-mentioned cross linking agent etc., heating if needed (preferably 40-150 degrees C), and performing crosslinking reaction, after making a solvent suspend a granulation object in a reaction vessel, Or a granulation object is made to fluidize by the fluid bed etc., subsequently the water solution of the above-mentioned cross linking agent etc. is sprayed, and the method of heating if needed (preferably 40-90 degrees C), and performing crosslinking reaction etc. is mentioned. Like ****, it carries out drying the granulation object with which the bridge was constructed over the front face which were obtained by carrying out if needed etc., and the target water-absorbing resin is obtained.

[0040] The above-mentioned base polymer particle consists of the above-mentioned granulation object which gathered and was formed, and a bridge is constructed over the front face, and the above-mentioned water-absorbing resin has the above-mentioned predetermined particle size. [two or more]

[0041] and excel in water absorption physical properties, and the parallel swelling coefficient of water absorption according [for example,] to the measuring method of the following ** - ** is desirable, 30-70 (g/g), and an initial water absorption rate are desirable, 5-15 (ml/30sec), and a dipping rate are desirable, and the above-mentioned water-absorbing resins obtained by the 1st invention and the 2nd invention of this invention are 20-150 (ml/min) -- etc. -- it has the outstanding property.

[0042] ** [Measuring method of an equilibrium swelling coefficient of water absorption]

Polymer 1g is distributed in a 200g physiological saline (0.9% brine). After making this polymer swell until the coefficient of water absorption will be in equilibrium, the mixed liquor of a polymer and a physiological saline is filtered at the wire gauze of 80 meshes. The weight (W) of the obtained swelling polymer was measured and the value acquired by *(ing) this value by the polymer weight (W0) before absorbing water, i.e., the value of W/W_0 , was made into the equilibrium swelling coefficient of water absorption (g/g).

[0043] ** [Measuring method of an initial water absorption rate]

Equipment Demand Wettability Tester shown in drawing 1 generally known as equipment which measures an initial water absorption rate It uses. the polymer spraying base (70mmphi --) set to water levels [oil level / of a physiological saline W] as shown in drawing 1 The coefficient of water absorption at the time of sprinkling 0.3g of polymers P and sprinkling a polymer on the base which put No.2 filter paper on glass filter No.1, is set to 0, and it is a coefficient of water absorption of 30 seconds after (this coefficient of water absorption). it measures with the graduation of the buret in which the amount of falls of the water level of a physiological saline W is shown -- having -- it measured and the initial water absorption rate (ml/30sec) was found.

[0044] ** [Measuring method of a dipping rate]

The equipment 10 (the bore of 25.6mm, glass cylinder filter with a cock with a die length of about 500mm (cylinder part)) shown in drawing 2 is filled up with polymer 0.5g. Make a polymer swell using a superfluous physiological saline, double an oil level with the place of 200ml from the lower part, and a cock is rebuked. Confirm that the swollen polymer P fully sedimented like illustration, and a cock is opened. The physiological saline W measured the time amount which passes through between (50ml of volume) the two marked lines L (it is a 150ml

point from the lower part), and M (it is a 100ml point from the lower part) shown in drawing, ******(ed) the volume between the marked lines (ml) by the measuring time (min), and considered as the dipping rate (ml/min).

[0045] [Example] Hereafter, although an example and the example of a comparison explain this invention to a detail, this invention is not limited to these.

[0046] In addition, the measuring method performed in the example and the example of a comparison is as the above-mentioned ******-****** and the following ******.

****** [Particle size distribution and measuring method of mean particle diameter]

Polymer 100g was classified using the JIS sieve, and it asked for particle size distribution and mean particle diameter from the weight fraction of each fraction.

[0047] [the example 1 of manufacture] -- 5l. 4 opening round bottom flask which attached an agitator, a reflux cooling pipe, and nitrogen installation tubing -- cyclohexane 1600ml and sorbitan monostearate -- [-- "-- LEO gold SP-S10" and the Kao Corp. make -- after having taught]5g, making it distribute and performing a nitrogen purge, the temperature up was carried out to 75 degrees C. Moreover, 560g of 30% of the weight of caustic soda water solutions neutralized 510g of 80% of the weight of acrylic-acid water solutions in another container, 0.4g of potassium persulfate was added to it with 30g of ion exchange water as an initiator, and the polymerization nature water solution was adjusted to it. And after dropping this polymerization nature water solution over 1.5hr(s) into the above-mentioned 4 opening round bottom flask and carrying out a polymerization under stirring, it held at the temperature of 70-75 degrees C for 0.5 hours, and the polymerization was made to complete. As a result of drying the obtained sodium-polyacrylate polymer particle and measuring particle size distribution and mean particle diameter, the particle with a particle size of 70 micrometers or less was 70% of the weight of a microparticulate sodium-polyacrylate particle group. Moreover, the moisture in this microparticulate sodium-polyacrylate particle group (water content) was 50 % of the weight.

[0048] [an example 1] -- the water content obtained by the approach of the example 1 of manufacture -- 50 % of the weight -- the particle not more than particle-size 70micrometer -- as 200g (base polymer particle group) of 70% of the weight of microparticulate sodium-polyacrylate particle groups, and a cross linking agent -- DENAKORU EX810[Nagase Brothers -- formation -- Industry -- for the kneader of 1l. capacity, stirring mixing was performed for 1 hour,]2g was dried after that, it cooled, and granulation ******** was obtained. Using shaking ********, like ********, it carried out, particle size distribution and mean particle diameter were measured, and the equilibrium swelling coefficient of water absorption, the initial water absorption rate, and the dipping rate were further measured about the obtained granulation object. The result is shown in [Table 1]. The end of a particle or a big and rough particle is not almost in the obtained granulation object, and it turns out that the manufacturing method of this invention is an approach excellent in granulation nature so that clearly from the result shown in [Table 1].

[0049] [Example 2 of manufacture] The microparticulate sodium-polyacrylate particle obtained by the approach of the example 1 of manufacture was dried further, and the polymer particle of 0.6 % of the weight of water content was obtained. As a result of measuring the particle size distribution of the obtained polymer particle, the particle with a particle size of 70 micrometers or less was 85% of the weight of a microparticulate sodium-polyacrylate particle group.

[0050] [Example 2] The particle with a particle size of 70 micrometers or less obtained by the approach of the example 2 of manufacture started stirring mixing of microparticulate sodium polyacrylate for 5000g of 85% of the weight of microparticulate sodium-polyacrylate particle groups for the "vertical granulator" of 25l. capacity [Powrex Make]. Next, it was dropped having poured 1200g of sodium-polyacrylate water solutions for 10 minutes 0.03% of the weight as a binder, stirring mixing was carried out for 10 minutes after that, and the granulation object was obtained. Particle size distribution were measured using shaking **** about the obtained granulation object. The result is shown in [Table 1]. Then, for the 5l. 4 TSU opening flask into which cyclohexane 1600ml was beforehand put for 500g of obtained granulation objects, the granulation object was made to suspend and the temperature up was carried out to 80 degrees C under stirring mixing. next, what dissolved "DENAKORU EX810" [product made from Nagase Brothers Industry] 1.5g in 10g of ion exchange water as a cross linking agent was dropped, and granulation **** which performs crosslinking reaction at 80 degrees C and by which the bridge was constructed over the front face of each granulation object was obtained. About the obtained granulation object, the same measurement as an example 1 was performed. The result is shown in [Table 1]. The end of a particle or a big and rough particle is not almost in the obtained granulation object, and it turns out that the manufacturing method of this invention is an approach excellent in granulation nature so that clearly from the result shown in [Table 1].

[0051] [Example 3] While the particle with a particle size of 70 micrometers or less obtained by the approach of the example 2 of manufacture fed 80-degree C air in equipment for the "multiplexer" of 10l. capacity [Powrex Make] by making 1000g of 85% of the weight of microparticulate sodium-polyacrylate particles into a base polymer, stirring by the impeller was performed, and a flow and stirring mixing of the above-mentioned microparticulate sodium-polyacrylate particle were started. Next, it was begun as a binder into the system to spray 1000g of sodium-polyacrylate water solutions 0.03% of the weight, and spraying of a binder was ended in about 40 minutes. Then, after spraying into the system held at 80 degrees C, having applied [which mixed "DENAKORU EX810" [product made from Nagase Brothers Chemicals Industry] 5.0g with 100g of ion exchange water as a cross linking agent] it for about 10 minutes, it dried with 85-degree C air for 30 minutes, subsequently it cooled, and the granulation object was obtained. About the obtained granulation object, the same measurement as an example 1 was performed. The result is shown in [Table 1]. The end of a particle or a big and rough particle is not almost in the obtained granulation object, and it turns out that the manufacturing method of this invention is an approach excellent in granulation nature so that clearly from the result shown in [Table 1].

[0052] [Example 4] It classified by high performance screen machine high BORUDA [New Tokyo Machine company make] to which the particle with a particle size of 70 micrometers or less obtained by the approach of the example 2 of manufacture set the screen of 30 micrometers of openings for 85% of the weight of microparticulate sodium polyacrylate. When the particle size of the obtained microparticulate sodium polyacrylate was measured with the particle counter [Coal tar company make], the particle with a particle size of 1-30 micrometers was 80 % of the weight. This microparticulate sodium polyacrylate was used, and also the granulation object was obtained like the example 3. Particle size distribution was measured using shaking **** about the obtained granulation object, and the same trial as an example 1 was performed. The result is shown in [Table 1]. Most impalpable powder or big and rough particles are not in the obtained granulation object, and it turns out that the manufacturing method of this invention is an approach excellent in granulation nature so that clearly from the result shown in [Table 1].

[0053] [Example 3 of manufacture] Sorbitan monostearate was replaced with ethyl cellulose (HAKYU lathe company make) 4g, and also the polymer particle group was obtained like the example 1 of manufacture. As a result of drying the obtained polymer particle group and measuring particle size, 70 micrometers or less were 5% of the weight of a polymer particle. Moreover, the moisture in this polymer particle group was 1.3 % of the weight.

[0054] [Example of a comparison] The particle with a particle size of 70 micrometers or less obtained by the approach of the example 3 of manufacture used 500g of 5% of the weight of microparticulate sodium-polyacrylate particle groups, and also the granulation object was obtained like the example 3. Particle size distribution was measured using shaking **** about the obtained granulation object, and the same trial as an example 1 was performed. The result is shown in [Table 1]. The obtained granulation object had many big and rough particles, and they were inferior to it also in water absorption physical properties.

[0055] [Table 1]

		実 施 例				比較例 1
		1	2	3	4	
造 粒 機 種		ニーダー	パーティカル グラニューター	攪拌転動 型流動層	攪拌転動 型流動層	流 動 層
平衡膨潤吸水量 (g/g)		3 8	4 2.5	4 4	4 0	4 2
初期吸水速度 (ml/30sec)		5.2	5.5	6.5	9.5	2.1
通 液 速 度 (ml/min)		3 5	2 7.6	1 1 6.9	8 5.6	1 7.3
粒 径 分 布 (μm)	<70	0	1.4	0.1	0.3	0
	70 ~ 106	0.5	3.6	3.6	4.3	0.2
	106 ~ 150	1.6	4.5	1 2.3	1 5.3	2.8
	150 ~ 355	8.9	1 9.3	3 2.6	3 3.8	5.6
	355 ~ 590	2 9.4	3 5.0	3 5.8	3 0.4	1 3.6
	590 ~ 1000	4 1.0	2 2.5	1 4.1	1 5.6	2 6.1
	1000~1500	1 2.5	1 0.6	1.3	0.3	2 9.3
	1500<	6.1	3.1	0.2	0	2 2.4

[0056]

[Effect of the Invention] The manufacturing method of the water-absorbing resin which can manufacture efficiently absorptivity resin with a high-speed water absorption rate or the high water-absorption-power force according to this invention is offered, and since the base polymer particle which has absorptivity in a detail, without applying compressive force and shearing force is corned and it is possible to obtain the granulation object of the porosity-ized indeterminate form, i.e., absorptivity resin with large surface area, the water-absorbing resin which improved the water absorption rate and the dipping rate greatly is obtained. Moreover, since a bridge is constructed over a base polymer comrade and a granulation object does not collapse at the time of contact in water, either, the water-absorbing resin to which gel blocking does not take place is obtained. Therefore, the water-absorbing resin obtained according to the manufacturing method of this invention can be used for broad fields including sanitary goods, such as a disposable diaper and a sanitary napkin.

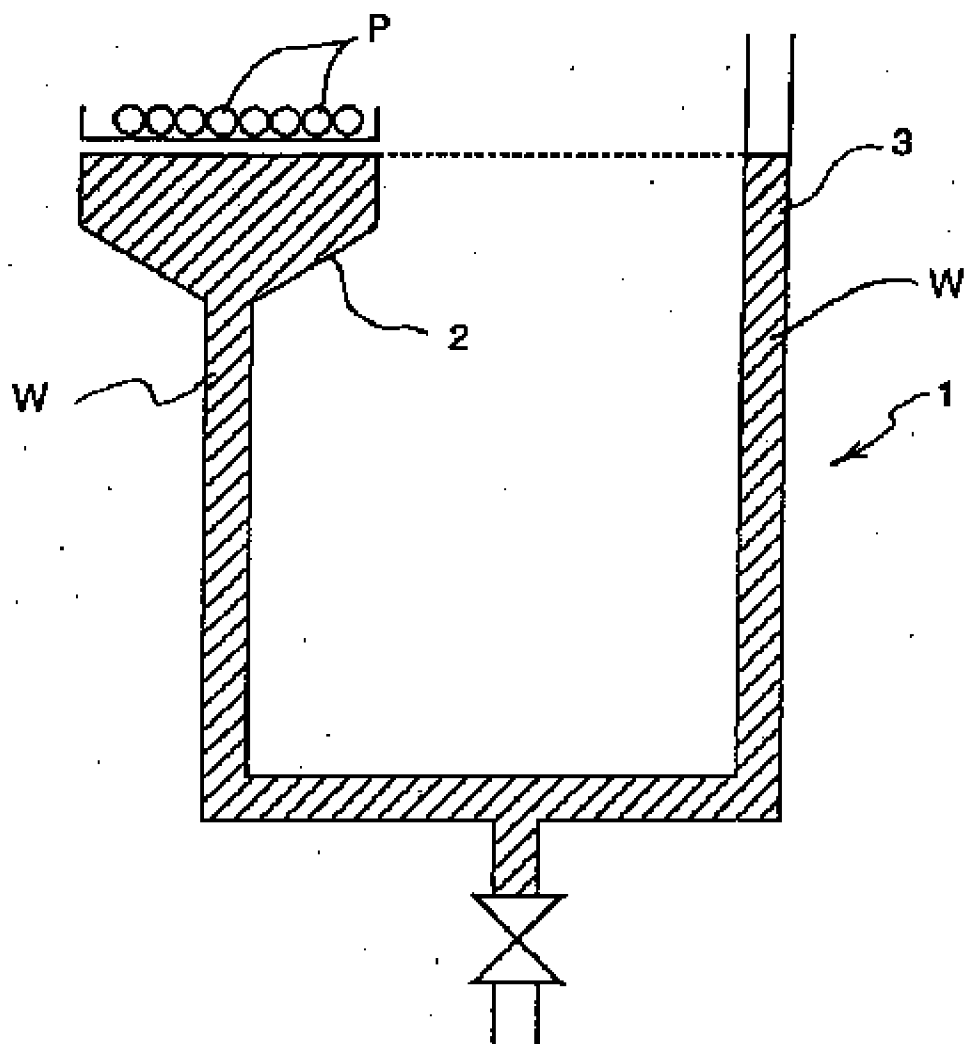


FIG 1

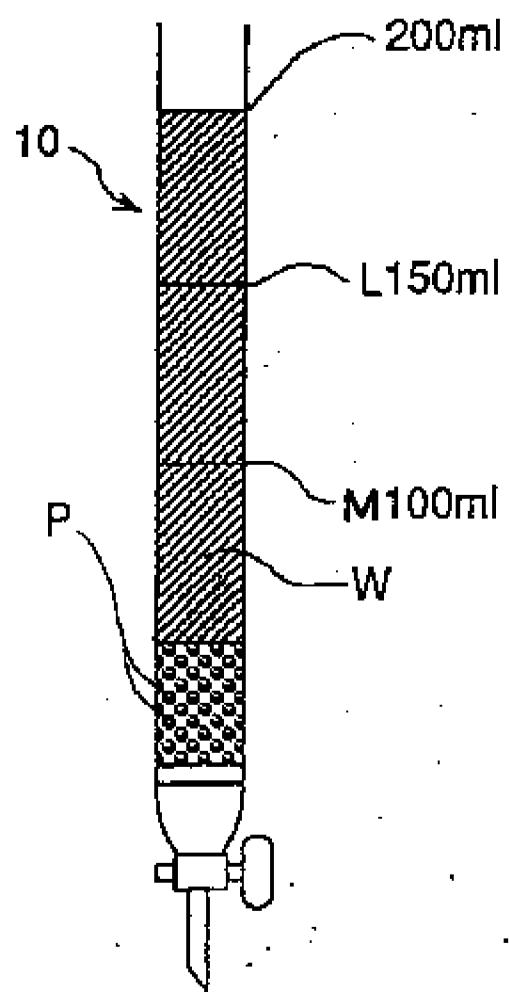


FIG 2